

# Lectures on Surface Science

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# Formation of Paramagnetic Centres on Surfaces of Zeolite Systems

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## 1. Introduction

The faujasitic zeolites are crystalline aluminosilicates of high porosity and are of wide use in petrochemistry. Generally, these synthesized zeolites possess organic compounds which under certain temperature and pressure conditions can build paramagnetic centres on the lattice surface. These centres can be of great importance in chemical reactions.

## 2. Sample Preparation

The samples were prepared from NaX zeolites synthesized by the University of Leipzig in Germany with a Si/Al ratio of 1.37, a  $\text{Fe}_2\text{O}_3$  content of less than 3 ppm and a carbon concentration of 0.12, gasometrically measured. Other paramagnetic impurities higher than 10 ppm could not be detected either in the NaX zeolite or in the other reagents used. The preparation of the zeolite samples was always done under high vacuum if not otherwise mentioned. The two prepared sample sets differ basically in the thermal pretreatment: one group was heated for two days at 260°C and the other group at 400°C. The ammonium exchange of the  $\text{NaX} \cdot (\text{DMSO})_d \cdot \text{NH}_4$ -zeolite system was 15%.

## 3. Experimental Results

The first sample set showed the following results:

- No EPR signal was observed in the original NaX zeolite that was thermally treated and sealed at room temperature at atmospheric air pressure (fig. 1, spectrum 2) or heated up to 260°C and sealed in high vacuum (fig. 1, spectrum 3). Similarly, both the NaX-DMSO- and the  $\text{NaX} \cdot (\text{DMSO})_d \cdot \text{NH}_4$ -zeolite systems exhibited no detectable paramagnetic signals if they were prepared and also sealed in high vacuum (fig. 1, spectrum 6 and fig. 2, spectrum 5). For the sample mentioned first, this result was verified by NMR pulse spectrometry /1/.
- On the contrary, the NaX-DMSO-zeolite system showed a structureless wide EPR line ( $\Delta H=1000\text{G}\pm 25\text{G}$ ; fig. 1, spectrum 4), if it was filtered and dried at atmospheric pressure and not sealed hermetically. The concentration of these paramagnetic centres was approximately  $N_p=10^{16} \text{ cm}^{-3}$  /2/. Two and a half months later, it was impossible to detect this signal again (fig. 1, spectrum 5). Nevertheless, eight and a half months before this measurement, the same air-sealed system had an impurity concentration of about  $N_p=10^{20} \text{ cm}^{-3}$ .
- Likewise, the  $\text{NaX} \cdot (\text{DMSO})_d \cdot \text{NH}_4$ -zeolite system showed a broad structureless EPR line ( $\Delta H=1000\text{G}\pm 25\text{G}$ ) with a  $N_p=10^{16} \text{ cm}^{-3}$  overlapped by a sharp free radical line ( $g=2.01$ ; fig. 2, spectrum 1). This sample was filtered and dried under atmospheric air pressure and not sealed hermetically. The broad line decreased continuously with time, leading finally after six months to a nearly constant value. Meanwhile, the free radical line had disappeared

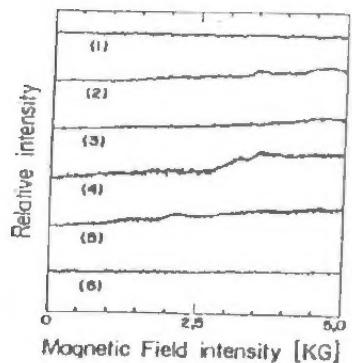
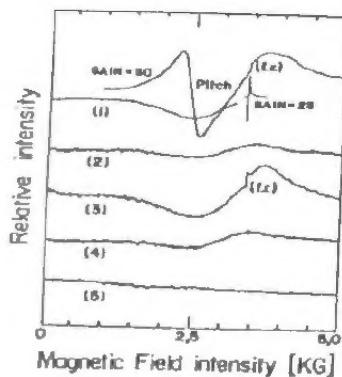


Fig. 1: EPR spectra of NaX- and NaX-DMSO-zeolite. Spectrum 1 is the background of the cavity.



Fin. 2: EPR spectra of the NaX-(DMSO)<sub>d</sub>-NH<sub>4</sub>-zeolite system.

completely (fig. 2, spectrum 2). If the same type of sample is sealed hermetically at atmospheric air pressure after its preparation the EPP signal maintains its intensity (fig. 2, spectrum 3). However, if the seal is removed and the system is not closed hermetically the broad line drops off after two months to nearly the value mentioned above. The sharp signal could not be detected after that time (fig. 2, spectrum 4).

The second sample set showed the following experimental data:

- a) The pure NaX zeolite displays no paramagnetic signal when it was heated

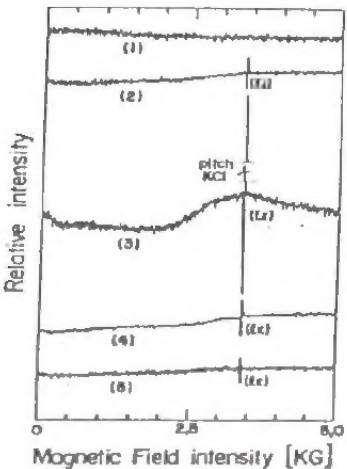


Fig. 3: EPR spectra of NaX-zeolites under different conditions of pre-treatment.

in air up to 400°C at a rate of 2°C/min and sealed at atmospheric air pressure and room temperature (fig. 3, spectrum 1). To the contrary, if this sample was warmed up again to 400°C with the same heating rate and in high vacuum a sharp free radical line and a broad line were observed. The signal-to-noise ratio of the broad line was too low to be analysed (fig. 3, spectrum 2).

b) Both above-mentioned EPR signals could be detected again in a NaX zeolite (fig. 3, spectrum 3) when the sample was warmed up in high vacuum with a heating rate of 15°C/min and hermetically sealed in high vacuum or atmospheric pressure. These two signals lost their intensities considerably when the heating rate was reduced to 2°C/min independent of the sealing procedure of the sample (fig. 3, spectra 4 and 5).

c) By means of mass spectroscopy the carbon monoxide desorption was studied, i.e. the reaction product of the organic molecules contained in the organic zeolite which desorbed with increasing intensity from 30°C to 200°C and drops off to zero at 250°C (fig. 4a).

d) With the same technique it was found that the water of an original NaX zeolite desorbs continuously between room temperature and 200°C with a maximum at 150°C (fig. 4b).

e) Using a calorimetric test /3/ it was possible to prove the presence of carbon monoxide in NaX zeolite samples heated up to 400°C in high vacuum.

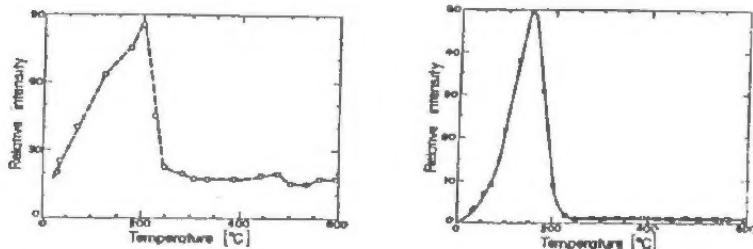


Fig. 4a(---) and 4b(—): Desorption curves of carbon and water of a NaX-zeolite.

#### 4. Discussion

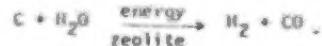
##### Samples heated up to 260°C:

Since the samples prepared and sealed under high vacuum showed an extremely low EPR signal, one has to conclude that the air presence generates and destroys the paramagnetic centres. This means that the formation of the broad paramagnetic signal in the NaX-DMSO- and in the NaX-(DMSO)<sub>0.5</sub>-NH<sub>4</sub>-zeolite systems has to be attributed to oxygen molecules being in contact with the inner zeolite surface. In these systems the broad EPR line conserves its magnitude when the samples are closed hermetically, and reduces its intensity with the time to a constant value when the samples are air filled. From these facts it has to be concluded that there are two opposing mechanisms in a NaX-DMSO-system: a fast one which creates paramagnetic centres and a slow one which destroys them. The reversibility of these processes suggests to postulate a physical adsorption of the oxygen molecules. The last assumption agrees with published results /4/. The reversibility is complete for the free radical centre and partial for the broad EPR signal which arrives finally at a dynamic equilibrium between the molecular oxygen complex and a molecular configura-

tion without paramagnetic effect. In the same way it is possible to explain the behaviour of the free radical signal, with the additional condition that these centres require a well-defined electronic structure and the presence of the  $\text{Mn}^{4+}$  ions that favours its generation and stability.

Samples heated up to 400°C:

For the interpretation of the experimental results of this set of samples the presence of carbon atoms in the zeolitic systems is decisive. If the NaX-zeolite is heated up to 400°C at atmospheric air pressure the carbon atoms oxidize completely to a non-paramagnetic carbon oxide, whereas this heating process in high vacuum form carbon monoxide. Simultaneously paramagnetic ions are produced, generating the broad EPR line as well as the sharp free radical peak, too. The concurrent desorption of the water and the carbon monoxide makes necessary to assume an incomplete oxidation of the zeolite included carbon according, for instance, to the following reaction equation:



Taking into account the high electric affinity of faujasitic zeolites for polar molecules, the presence of the carbon monoxide up to 400°C in the sample has to be correlated with the electrical local fields which are produced by defect charges in the crystal structure and are able to adsorb strongly CO molecules. The increase of the paramagnetic signals with increasing heating rate of the samples under maintained vacuum agrees with the above-mentioned assumption because the readsorption of the carbon is faster now. Furthermore, it can not be excluded that the heating procedure in high vacuum up to 400°C produces coke particles which causes readsorption of CO, leading to an increase in the concentration of paramagnetic centres.

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